Abstract
Release agents for rubber moulding operations have been in use since the early days of rubber production. Neglected in the beginning as a necessary evil, these materials have developed over time to a much higher technology level, which this paper is going to focus on, as well as on the environmental impact of these systems.

Introduction
Rubber parts, produced in moulding operations, have always faced two main obstacles: First, to get the mould sufficiently filled with compound and, second, to remove the finished product from the mould.

This presentation is going to focus on the second problem, the removal of the moulded and vulcanized product and the technologies involved to facilitate this process step.

Mould release agents belong to the category of products, widely looked upon as “can product” or “I don’t like you, but I need you”.

The reasons for these resentments are multiple:

- Release agents require an extra step in the production process
- They can interfere with the compound flow in the mould, which may lead to poor knitting
- Depending on the type of material being used, they can cause mould fouling
- They may interfere with the product surface, thus causing poor adhesion and poor printability
- Volatile matters, contained in the product, affecting work place and environment

For manufacturer of release agents, the challenge has been since the early days of simple release agents, such as oils, silicones, waxes, soaps, etc., to further develop products with reduced or eliminated side effects.

I do not want to spend much time on the historical development of mould release agents; just a brief classification of currently available products.
Classification of release agents

**Single use release agents**

This group consists predominantly of non-reactive silicones, soap solutions/suspensions and oils. If we include tyres as moulded parts, the products may even include solids, such as clay, mica, etc. The materials are commercially available or even still ‘in-house’ produced, as some small and medium size tyre manufacturer still do.

The release function of these products can be explained by cohesive failure in the release film when the rubber part is being removed from the mould\(^1\). This implies, that a certain amount of release agent is left on the mould surface, which causes most of the failures and problems, I have mentioned before.

**Permanent release agents**

During the Seventies, several attempts were made, to coat mould surfaces with a permanent release film, supposed to last the lifetime of the mould.

One material used was PTFE (polytetrafluorethylene) . It turned out to be not very practicable. Admittedly, the release effect of PTFE is very good, however, a certain degree of slip needs to be present to aid compound flow in the mould. PTFE coatings, in the opposite, created a rather rough surface, which leads to a very fast wear-off, due to the abrasive nature of most filler containing compounds. Consequently, these systems never became commercially viable on a wider scale.

**Semi-permanent release systems**

Semi-permanent release agents are designed to achieve multiple releases with one surface treatment.

They form a thin, but resistant layer on the mould, that will not be transferred to the surface of the rubber parts.

This becomes possible through the development of crosslinkable polymer systems that can be used in a liquid carrier. The carrier can be based on solvents or water.

After application of a thin layer onto the hot mould surface, a film forms through evaporation of the carrier and by crosslinking at the same time.
The adhesion of the film to the metallic surface can be explained by the effect of "Van der Waals' forces".

Due to the characteristics of the film, the single release effect might be slightly reduced, compared to single use agents (like silicone), but this minor drawback is largely compensated by the numerous advantages of this system:

- Virtually no transfer to the part surface
- Prevention of residue build-up on the mould
- Provides true multiple releases
- Heat stability

Semi permanents, in their early stages, were based on solvent carrier that provided excellent film formation and uniformity and could even be applied at lower mould temperatures.

The main problems of these products were the environmental impact and the health and safety in the workplace.

Fortunately, most countries have outlawed CFC containing solvents, but highly flammable materials, such as aliphatic hydrocarbons, replaced these; which shifted the hazardous part from one side to the other.

Regulation and increased conscience finally lead to not only the development of water-based materials, but also to their rapidly increasing use.

Today a range of environmentally safe products is available to the industry that is technically equivalent, if not better, than the solvent-based materials.

In this paper, we do not wish to elaborate on the development and formulating part of water based semi-permanents, since this is in most cases based on similar building blocks, like surfactants and the polymers itself. The know-how differences are in achieving the right balance between surfactant and types of polymers, which ultimately influences the performance of the product. Usually a catalyst is added to increase the crosslinking speed.

Before we go into the application of Semi-Permanent Release Agents, I would like to mention a relatively recent development in this field, based on **Nano Particle Technology**. 
Nano particles are usually metal oxides, for this particular application ZrO$_2$, TiO$_2$, ZnO and alpha – Al$_2$O$_3$.

The particle sizes range from 5 up to 90 nm.

Through fluorination of nano particles, the resulting material can be applied to a surface where the fluoro particles re-organize themselves towards the exposed surface, thus forming a durable release film.

As intriguing this new technology appears, due to the production technology and the cost involved, we do not expect it to replace standard semi-permanents anytime soon.

**Application of Semi-permanents**

The most important step for the application of any kind of semi-permanents is the proper cleaning of the mould. This is absolutely essential for a proper adhesion of the coating to the mould surface.

Next important is the application temperature!

With water based semi-permanents, the temperature is somewhat restricted to a minimum of preferably above 90$^\circ$ Celsius, in order to evaporate the water as fast as possible.

This is important for two main reasons, to start the crosslinking of the film and to prevent corrosion of the mould surface.

Here, the basic rule applies: The higher the temperature, the shorter the crosslinking time. Since moulding of rubber takes place at or above 140$^\circ$ C ~ 150$^\circ$ C, the crosslinking times for the film are relatively short, 10 minutes or even less, depending of the catalyst being used in the product.
This pre-requisite makes the use of water-based products for low temperature moulding (e.g. PU), difficult if not impossible.

The coating can be applied in different ways, e.g. brushing, wiping or spraying. Spraying is, however, the most commonly used method, which also ensures the most even and uniform film formation.

Semi-permanents should be applied as sparingly as possible; the thinner the film, the more stable and even it will be. After the crosslinking of the first coating, a second layer may be applied. This is mainly to help leveling out irregularities in the mould surfaces, as there are tiny scratches, cavities, etc. It is self understood, that there are limits to what a release agent can do! It does certainly not repair damaged moulds.

After these steps, the mould can be put into service. If there is no previous experience with semi-permanents, it is advisable to closely monitor the curing cycles until the release effect diminishes. Now the point of re-application is reached.

This can be done ‘in situ’, without cleaning or removing the mould, by simply re-applying one thin film. Semi-permanents prevent material built-up in the mould for extended periods (as compared to non-permanent release agents).

These was shown in studies, using methods of surface analysis (e.g. X-ray spectroscopy) to determine the type and amount of built-up after multiple curing cycles. With semi-permanents, it was clearly shown, that whatever volatiles come out of the compound, it will hardly be transferred to the mould ².
The re-application procedure can be repeated to the point where the material residue in the mould reaches a level that prevents a proper film adhesion. The mould has then to be removed for a standard cleaning procedure.

Now we come to the thorny question:

**How many curing cycles can I achieve without cleaning my mould?**

And the stereotype answer is “It depends….!”

And on what does it depend? Several main factors will affect the mould life between cleaning cycles:

- **The polymer base of the compound.**
  It is well known, that halogenated polymers tend to stick much more to metallic surfaces than standard polymers. Good (bad) examples are FKM, ECO, ACM, CR,….
  The numbers of curing cycles to cleaning are considerably lower with these compounds than, for example, for SBR, NR, BR, NBR,….

- **The type of filler.**
  More abrasive fillers, like most mineral filler types, are promoting faster wear on the coating than softer fillers like carbon blacks.

- **The curing system.**
  Accelerator systems or the complexes formed by them can be volatile and might attack the release film. Peroxide systems are especially infamous for such effects.

From experience, moulding cycles can be as many as several hundreds, down to as little as fifty, depending on the above-mentioned factors.
Conclusion

Semi-permanent release agents offer a wide range of advantages over non-permanents:

- Reduction of down time, since application after each cycle is not necessary.
- Prevention of mould fouling
- Much extended intervals between mould cleanings.
- Extreme reduction of flow faults caused by entrapped release agent during the mould filling process (poor knitting)
- No adverse effect on the surface of the finished part with regards to painting, printing or bonding!

Consequently, this will all result in a reduced scrap rate, which can be counted in money.

Since there are differences in polymers, fillers, mould shapes, a range of different products have to be made available with different properties.

A typical range of water-based semi-permanents consists of a minimum of four standard grades, mostly variations in concentration and types of polymers used.

The above-mentioned technical advantages, combined with the environmental aspect, make water-based semi-permanents a must for the responsible moulding operator.

References:

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